Evaluation Report for the Feasibility Study Solidification/Stabilization of Arsenic Containing NSCMP Neutralents

Prepared for:

Non-Stockpile Chemical Materiel
Program Manager

Contract No.: DAAM-01-96-D-0010

Stone & Webster, Inc.
A Shaw Group Company

February 2002

EVALUATION REPORT

Evaluation Report for the Feasibility Study Solidification/Stabilization of Arsenic Containing NSCMP Neutralents

Prepared for

United States Army

Non-Stockpile Chemical Materiel Program Manager

Chemical Demilitarization Project

Report No. R37-V-08

Revision 0

February 2002

S. Austermann
Dr. J. M. Cardito
N. L. Nemser
C. A. Freedlund

Approved By: _____
Stone & Webster Project Manager

Government Release By: _____
NSCMP Task Manager

EXECUTIVE SUMMARY

This is the evaluation report of the Feasibility Study for Solidification/Stabilization of arsenic containing Non-Stockpile Chemical Materiel Program (NSCMP) neutralents. Testing was performed at Southwest Research Institute (SwRI) in San Antonio, Texas. Stone & Webster Stone & Webster conducted these tests on behalf of NSCMP (Edward F. Doyle, Alternative Systems Demonstration and Evaluation Group Leader) to assess whether solidification/stabilization is a suitable treatment of arsenic containing NSCMP waste prior to disposal in a landfill.

This test program focuses on RRS RED neutralent, which due to its volatile organic nature, was considered the most challenging NSCMP arsenic containing waste to solidify. The predominant compound in the RRS RED neutralent is chloroform, at an estimated concentration of 60%. Both chloroform and arsenic (As) fall under strict hazardous waste management regulations.

The test methodology was based on the findings of a literature search that included recent successes in the solidification of liquid organic compounds. Two different approaches for solidifying the material were investigated by SwRI;

- Solidification/Stabilization of the entire organic-liquid-based waste stream, and
- Distillation and recovery of the organic solvent (e.g. chloroform) and then subsequent separate stabilization of both the organic overhead distillate and the arsenic containing bottom fraction prior to solidification in concrete.

For the solidification/stabilization of the entire stream, a “two step” process was initially tested as the first approach. In the first step, the simulant was adsorbed onto a mixture of crumb rubber and silica. In the second step the resulting product was incorporated into a high strength concrete.

Initially, the “two-step” process was applied to the entire RRS RED neutralent simulant. This process however proved unsuccessful, and was abandoned.

In the second approach the neutralent was distilled to separate the chloroform fraction from the remaining neutralent. The top fraction of the distillation contained predominantly chloroform (>90%). Due to the unsuccessful results of the first “two-step” approach, which was assumed to be attributable to the high chloroform concentration, it was decided to attempt to react the chloroform rich phase with a toluene-polystyrene mixture for stabilization. The resulting polymer was then solidified in a Portland cement matrix together with a proportional amount of Bottom sample, which was stabilized using the two-step method. The TCLP analysis following a 27 day curing period, showed a good retention for arsenic however the chloroform, benzene and mercury concentrations in the leachate exceeded the regulatory limits, as stated in 40 CFR 261.20 (TCLP) and 40 CFR 268.48 (Universal Treatment Standards).

As part of a separate test program also performed at SwRI, RRS RED neutralent was treated using persulfate oxidation. The analyses indicated that the arsenic remained in the aqueous liquid. It was therefore decided to solidify/stabilize the oxidized RRS RED neutralent residual. The subsequent TCLP analysis showed that none of the RCRA regulated metals including arsenic was detectable in the leachate.

- Since the screening tests for solidification/stabilization of the entire RRS RED neutralent simulant stream were not successful, it is recommended not to investigate this option further.
- The stabilization of the As-containing distillation bottom fraction as well as the polymerization of the As-free overhead fraction were unsuccessful, due to the leaching of mercury, benzene and chloroform respectively. It is therefore recommended to consider a different method for the disposal of the chloroform rich overhead fraction. The solidification of the bottom fraction especially with respect to the retention of mercury should be investigated further.
- If the oxidation of the RRS RED neutralent is pursued further, then the solidification/stabilization of the resulting effluent should be investigated further.

Table of Contents

List of Tables

List of Figures

Evaluation Report for the Feasibility Study of Solidification/Stabilization of Arsenic Containing NSCMP Neutralents

1.0 INTRODUCTION

This report is an evaluation of the Solidification/Stabilization test program conducted by Southwest Research Institute (SwRI) in San Antonio, Texas.

This test program was designed to determine the applicability of solidification/stabilization methods to arsenic containing Non-Stockpile Chemical Materiel Program (NSCMP) waste streams. The disposal of arsenic (As) falls under strict RCRA regulations, which require treatment prior to landfill in order to meet land disposal restrictions. Solidification/stabilization (S/S) is one of the standard treatment methods used for arsenic containing wastes. The established methods, such as in "Project Swiftsure" for the Canadian Department of National Defence [1], are based on immobilizing inorganic arsenic salts in aqueous systems. Applying S/S methods to organic waste streams, such as the RRS RED neutralent, is a new concept with little information reported in the literature. It was therefore decided to concentrate this test program on the RRS RED neutralent, which due to its volatile organic nature was considered the most challenging NSCMP arsenic containing waste stream to solidify/stabilize.

SwRI conducted the test program under a subcontract to Stone & Webster, Inc. (Stone & Webster) at their Chemistry and Chemical Engineering Division, Environmental Engineering Laboratory using standard equipment.

Due to the uniqueness of the waste stream and lack of previous experience with S/S of a high concentration organic stream, a literature search was performed to obtain the most up to date information in this area. This provided a basis for the test approach and the subsequent test plan development. The test approach chosen is detailed in Section 1.3.

The sections below discuss the test objectives of this Feasibility Study, the criteria Stone & Webster developed to evaluate the S/S methods investigated and the feed streams considered. Section 2 provides a summary of Stone & Webster's technology evaluation efforts and the rational for selecting S/S methods for bench scale testing. Section 3 is a summary of the Literature Search conducted by SwRI as part of this Feasibility Study to determine suitable solidification/stabilization methods. Section 4 describes the test methods used in this study and the observations made for each of the experiments. The results of the tests are presented in Section 5 of the final report, which includes the analytical results of the samples collected during testing. Sections 6 and 7 include the test conclusions and recommendations for further action.

1.1 Test Objectives

The principal objective of the investigation described in this report is to identify processes for the direct solidification/stabilization of arsenic containing RRS RED neutralent. The laboratory scale tests are to assess the effectiveness of solidifying/stabilizing organic based

RRS RED neutralents relative to RCRA land disposal criteria as stated in the Toxicity Characteristic Leaching Procedures (40 CFR 261.20) and the Universal Treatment Standards (40 CFR 268.48) and. Table 1-1 states the specific objectives and evaluation criteria that were applied to determine the success of the tests.

Table 1-1 - Test Objectives & Assessment Criteria

Test Objectives	Evaluation Criteria
a) Demonstrate the effective solidification/stabilization of arsenic containing RRS RED neutralent using selected media and methods.	• Cured concrete samples to pass TCLP, ignitability, corrosivity and reactivity in accordance with 40CFR261.21-24 and land disposal criteria at 40 CFR 268.48 (Universal Treatment Standards)
b) Determine the most suitable procedure by evaluating available materials and methods including pre-treatment	• Procedure • Handling, availability & cost of material
c) Provide basic data to evaluate the practicality of solidification/stabilization procedures for implementation in the NSCM Program	• Procedure • Recipe • Handling, availability & cost of material • System operating characteristics • System safety • Permitability

1.2 Feed Streams

There are potentially two major arsenic containing neutralents within the NSCMP: the aqueous based Lewisite neutralent and the RRS RED neutralent from the treatment of vials from Chemical Agent Identification Sets (CAIS). Neat Lewisite agent is neutralized by oxidizing it to an inorganic arsenic salt[2]. Solidification/stabilization processes for these salts are well established in programs such as "Project Swiftsure" carried out by the Canadian Department of National Defence as part of their chemical demilitarization program. The S/S of this feed stream therefore does not require further development.

This program concentrates on neutralent from the Rapid Response System (RRS). This system is used for the neutralization of CAIS vial sets. The sets contain Lewisite as well as Mustard filled vials, both in chloroform solutions. In the RRS these sets are treated with a DCDMH, t-butyl alcohol and chloroform mixture, which explains the organic nature of the stream.

This S/S test program used both simulant to determine the effectiveness of a method and actual neutralent for verification.

Stabilizing the organic compounds, mainly chloroform, was the first major objective of the test program. Since the S/S of organic based feeds was considered a major challenge, it was decided to prepare and test an RRS simulant without an arsenic component. After successful solidification/stabilization of the simulant, the arsenic would be added. Table 1-2 lists the composition of the different feeds proposed for this test program.

Table 1-2 - Feed Stream Specification

RRS RED Neutralent Components[3]	Wt%	Simulant Composition	Arsenic Simulant Wt %	Non-Arsenic Simulant Wt %
Chloroform	60-61	Chloroform	63.8	64.9
t-Butyl alcohol	17-20	t-Butyl alcohol	19.7	20.0
Chlorobutanes	1.2-4.6	1-Chlorobutane	1.6	1.6
		2-Chloro-2-methylpropane	1.6	1.6
1,3-Dichloro-5,5-dimethylhydantoin	0-4.6	1,3-Dichloro-5,5-dimethylhydantoin	4.5	4.6
Chloro-5,5-dimethylhydantoin	1.9-5.6	None	0	0
5,5-dimethylhydantoin	0-4.6	5,5-dimethylhydantoin	4.5	4.6
Chlorinated sulfoxides	0.6-2.1	Ethanesulfonylchloride	1.5	1.53
Chlorinated sulfones	0-0.06			
bis-(2-chloroethyl)amine	0-1	2-Chloroethyleamine hydrochloride	0.53	0.54
Chlorovinylarsonic acid	0-2.6	Cacodylic Acid	1.20	0
		Arsenic ethoxide	0.5	0
1,1,2-Trichloroethane	0-0.23	1,1,2-Trichloroethane	0.13	0.13
Tetrachloroethane	0-0.2	1,1,2,2-Tetrachloroethane	0.11	0.11
Acetaldehyde and chloroacetaldehyde	0-0.5	Acetaldehyde	0.11	0.11
		2-Chloroacetaldehyde	0.22	0.22
glass and plastic	7.5-10	None	0	0

1.3 Test Approach

A sequential approach was chosen for this task . A literature survey was carried out initially to identify successful solidification/stabilization methods for similar applications. The search concentrated on methods for the treatment of organic (mainly chloroform) and arsenic compounds, as both chloroform and arsenic are strictly regulated by RCRA Universal Treatment Standards. The high concentration of chloroform in the feed stream determined the two basic approaches selected for further investigation;

1. Solidification of the total stream
2. Separation by distillation of the neutralent into two fractions. The fraction separation temperature for the distillation would be selected to ensure the maximum separation of the chloroform from the arsenic-containing distillate. An initial distillation was designed to determine the cut-off point between the chloroform and the higher boiling components. The distillation also provided information about the distribution of arsenic. The distillation was followed by the separate S/S of the two fractions;
    a) S/S of bottom fraction using methods established in the first approach.
    b) Chemical reaction of the chloroform to incorporate it into a polymeric structure.

2.0 BACKGROUND

The U.S. Army Program Manager for Chemical Demilitarization (PMCD) established the NSCMP with the mission to provide centralized management and direction to the Department of Defense for the disposal of non-stockpile chemical materiel in a safe, environmentally sound and cost effective manner. The NSCMP includes five categories of chemical warfare materiel (CWM): binary chemical weapons; former production facilities; miscellaneous CWM; recovered chemical weapons; and buried CWM. Substantial differences exist between CWM in the Stockpile and Non-Stockpile programs. Whereas the stockpiled CWM is present in larger quantities, non-stockpile CWM encompasses a greater variety of materiel with far more physical configurations and agent-fill types. The variety, locations and deteriorated physical condition of non-stockpile CWM pose unique requirements for treatment systems.

To support accomplishment of its mission, the NSCMP developed an Overarching Research Plan[4] (ORP) which establishes the goals, requirements, and approaches for evaluating and developing technologies for the safe and efficient disposal of non-stockpile CWM. The ORP identifies systems that NSCMP has and is continuing to develop to meet its mission goals. The ORP also identifies additional needs and associated schedule to support accomplishment of these goals. The ORP identified Near-Term, Intermediate-Term and Long-Term applications for technologies to treat the broad range of NSCMP wastes.

To meet these needs, NSCMP has identified several additional systems for application to non-stockpile CWM based on the results of technology evaluations and demonstration testing performed as part of the PMCD Alternative Technologies and Approaches Program (ATAP) and the Assembled Chemical Weapons Assessment Program (ACWAP).

In support of these NSCMP activities, Stone & Webster is conducting Engineering Design Studies and other tests of several technologies for the treatment of NSCMP neutralents. The technologies under investigation typically treat the neutralent to produce non-toxic waste streams that can be disposed of without further treatment. This, however, is not the case when processing arsenic containing neutralent, as the resulting wastes require further treatment, such as solidification/stabilization before disposal is environmentally acceptable. The test program described herein investigates the efficacy of direct stabilization of the arsenic containing neutralent.

The starting point for this study is the work conducted under “Project Swiftsure” conducted by the “Defence Research Establishment Suffield” (DRES) for the Canadian Department of National Defence (DND)[1]. In this program Lewisite is oxidized with hydrogen peroxide to arsonic acid and subsequently sodium hydroxide is used to decompose the acid to arsenate salt. The arsenate/chloride salt slurry was then stabilized in a concrete mixture. Experiments to determine a suitable concrete mixture were carried out and the subsequent leachate tests complied with Alberta environmental standards.

The NSCMP program faces the same issue regarding the arsenic in the RRS RED process neutralent. This process treats CAIS vial sets containing Lewisite and Mustard in Chloroform, with a DCDMH solution. Due to the organic nature of the neutralized stream the

"Swiftsure" solidification method, which is based on arsenate salts in aqueous solutions, can not be applied, therefore alternative procedures had to be investigated.

Stone & Webster in cooperation with its subcontractor SwRI developed a scope of work to investigate methods to solidify/stabilize this organic based arsenic containing neutralent. Stone & Webster conducted the tests on behalf of NSCMP (Edward F. Doyle, Alternative Systems Demonstration and Evaluation Group Leader) to assess whether solidification/stabilization is a suitable treatment of arsenic containing NSCMP waste.

3.0 LITERATURE REVIEW

A literature review was performed by SwRI to investigate previous solidification/stabilization efforts for both organic and arsenic containing wastes. The findings from this report formed the basis for the test approach chosen and subsequently the test plan developed by Stone & Webster in cooperation with SwRI.

3.1 Definitions

The definitions for "stabilization" and "solidification" used for this report are those applied by the U.S. Environmental Protection Agency (EPA).[5]

- *"Stabilization* refers to those techniques that reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile, or toxic form. The physical nature and handling characteristics of the waste are not necessarily changed by stabilization."
- *"Solidification* refers to techniques that encapsulate the waste in a monolithic solid of high structural integrity. The encapsulation may be of fine waste particles (microencapsulation) or of a large block or container or wastes (macroencapsulation). Solidification does not necessarily involve a chemical interaction between the wastes and the solidifying reagents, but may mechanically bind the waste into the monolith. Contaminant migration is restricted by vastly decreasing the surface area exposed to leaching and /or by isolating the wastes within an impervious capsule."

3.2 Solidification/Stabilization of Arsenic compounds

The general method applied to solidify/stabilize metallic compounds is to convert them into oxides that are insoluble in basic pH solutions. Cement has proven to have a large capacity for maintaining a high pH in water that it contacts. Another advantage of solidification in a cement matrix is the low porosity of the final product, which reduces the contact between its internal constituents and the water on the surface.

Arsenic compounds are considered to be among the most difficult of all metallic species to be stabilized and solidified. However, they have been stabilized and solidified successfully. Arsenic compounds exist in two oxidation states, which can change in response to environmental conditions. In general oxides in the highest oxidation state are the least likely to leach out, which is also true for arsenic. In order to prevent arsenic species from converting to a lower oxidation state several additives can be mixed into the cement. One of the possible additives is ferric oxide, which is already present in Portland cement. Whether the amount of ferric oxide present is sufficient to stabilize the arsenic in the RRS RED neutralent feed stream will be determined experimentally as part of this project. The general procedures for the solidification/stabilization of arsenic oxides as well as other metallic compounds are well established.

3.3 Solidification/Stabilization of Organic Compounds

In the past, volatile organic compounds have not been regarded as suitable for stabilization and solidification technologies. Many organic materials interfere with Portland cement, and solidification/stabilization has been unsuccessful due to the volatile nature of the compounds.

3.3.1 "Two Step" Method

Only recently has a method been demonstrated as effective for the treatment of dilute volatile organic compounds[6,7]. The uniqueness of this approach is that the organic liquid is adsorbed onto a silica/crumb rubber mixture prior to being incorporated into concrete. This prevents any interference of the organic material with the Portland cement.

3.3.2 Chemical Reaction - Polymerization

The literature mentions that there is a possibility of incorporating organic compounds into a polymeric structure[8]. Most previous work in this area has applied a pre-polymer with the objective of physically absorbing the contaminant into the polymer without waiting for slow diffusion through the bulk, cured polymer matrix. However, many monomers themselves are highly reactive and are expected to react with waste constituents.

SwRI suggested the use of polystyrene pellets dissolved in neutralent, due to its high chloroform concentration, or toluene for the polymerization reaction. They postulated that a Friedle Crafts reaction would take place with aluminum chloride catalyst addition. Details of this chemical reaction are explained in Section 4.2.3.1 and Figure 4-10.

3.4 Literature Review Conclusion

The information found in the literature formed the basis for the test plan developed for this program. Two different approaches for solidifying/stabilizing the material were investigated by SwRI. The first approach evaluates the S/S of the entire stream using the "two-step" method detailed in Section 3.3.1.

For the second approach it is attempted to distill and recover the solvent (i.e. chloroform) and then separately solidify/stabilize the two fractions. It is anticipated that most of the chloroform is found in the overhead fraction while the higher boiling compounds including the arsenic remain mainly in the bottom fraction.

After the distillation the bottom fraction is stabilized using the "two-step" method and the overhead fraction is polymerized. If the resulting polymer proves to be sufficiently hardened for direct landfill it would undergo TCLP analysis; if not, the polymer would be incorporated into a Portland cement matrix prior to TCLP analysis. A detailed description of the tests performed including procedures, observations and results are given in the next section.

4.0 TEST DESCRIPTION

This section presents descriptions of the laboratory tests carried out at SwRI's facility in San Antonio, Texas as part of this feasibility study. The tests were conducted from June to December 2001. The test descriptions include discussions of the feed streams tested, the experimental set-up and procedure, and the sampling and analysis conducted. As part of this test program the following sets of experiments using both RRS RED neutralent and neutralent simulant were performed:

- Solidification/Stabilization of the complete neutralent stream using the "two-step method" – two non-arsenic simulant batches were prepared
- Distillation of the RRS RED neutralent to separate and recover the organic solvent (i.e. chloroform) fraction.
- Solidification/Stabilization of the neutralent distillation bottom fraction simulant using the "two-step method"
- Solidification/Stabilization of the chloroform rich distillation top fraction using polymerization followed by incorporation into a Portland cement matrix

4.1 Solidification/Stabilization of the Complete Neutralent Stream

The literature review indicated that a "two-step" method had potential. As part of this procedure the organic neutralent stream is adsorbed onto a crumb rubber/silica mixture prior to being solidified in Portland cement.

4.1.1 Simulant of Complete Neutralent Stream

Stabilizing the organic compounds, mainly chloroform, was the first major objective of the tests. It was therefore decided to prepare a simulant consisting only of chloroform and other organic compounds present in the neutralent. Only after successful solidification/stabilization of the non-arsenic simulant would an arsenic containing simulant be tested, to avoid unnecessary handling of a highly hazardous substance. Table 4-1 lists the composition of the simulant feed used in this initial test.

Table 4-1 – Non-Arsenic Simulant Feed Stream Composition

Simulant Composition	Non-Arsenic Simulant Wt %
Chloroform	65.12
t-Butyl alcohol	20.65
1-Chlorobutane	1.68
2-Chloro-2-methylpropane	1.6
1,3-Dichloro-5,5-dimethylhydantoin	4.56
5,5-dimethylhydantoin	4.6
Ethanesulfonylchloride	1.52
1,1,2-Trichloroethane	0.13
1,1,2,2-Tetrachloroethylene	0.11
Acetaldehyde	0.03

4.1.2 Test Matrix

The stabilized mixture contained a total of eight variable components: fumed silica, granular silica, crumb rubber, lime, simulant, sodium metasilicate, Portland cement and water. These result in 7 ratios as shown in Table 4-2, which were established during the tests. For the sorbent not only the silica to rubber to lime ratios had to be determined but also the amount of granular silica in relation to fumed silica. In the second step, after the sorbent to simulant ratio had been determined the concrete to additive to water mixture was established. A base case was selected to reflect both literature values and previous experience at SwRI. Each ratio in turn was changed to the value in Table 4-2 while keeping the others at base case values to observe the possible effect. This resulted in the following cases: high granular silica, high RRS RED neutralent, high silica, high rubber, high Portland cement, omit sodium metasilicate (NaMS) and low lime concentration. The ratios chosen for both the base case and the alternative cases are summarized in Table 4-2.

Table 4-2 - Basis for Trial Composition

Ratio Definition	1st Batch –Total		2nd Batch – Total		Bottom Fraction	
	Base Case	**Alternative Cases**	**Base Case**	**Alternative Cases**	**Base Case**	**Alternative Cases**
P. Cement: Total[a]	0.18	0.25	0.21	0.26	0.46	0.52
Water: (P. Cement + NaMS[b])	0.42	adjusted [c]	0.42	adjusted [c]	0.42	adjusted [c]
RRS Simulant: Sorbent[d]	0.67	Max[e], 0.33	0.67	Max[e], 0.33	1.89	3.7, 0.99
Silica: Rubber	1.2	0.8, 1.6	0.8	0.5, 1.2	1.2	0.8, 1.6
Lime[f]: Silica	0.25[g]	0.10[g]	0.25	0.10	0.25	N/A
Fumed Silica: Granular Silica	1.35	0.65	1.35	0.75	1.35	0.65
Sodium Metasilicate: Total	0.08	0.00	0.08	N/A	0.08	0.00

a. The total concrete composition includes water, simulant neutralent, and sorbent.
b. Sodium metasilicate.
c. The water quantity was adjusted for each sample to ensure ideal consistency of the concrete sample for curing process.
d. The sorbent composition includes fumed silica, silica flour ("granular"silica), lime (calcium hydroxide), and crumb rubber.
e. The apparent maximum for making a viscous paste, arbitrarily assumed to be 1.0 for planning. Following determination of the actual maximum in the initial experiment, the other ratios were adjusted proportionately.
f. Lime as calcium hydroxide.
g. Lime not included in samples for first batch, although initially planned

Portland cement contains a number of additional compounds including calcium oxide and either silica, alumina and/or ferric oxide. The addition of water causes rapid formation of calcium hydroxide, which then forms calcium silicate complexes that hydrate slowly, consume the water and precipitate as crystals. These crystals facilitate the hardening of the concrete mixture.

Organic compounds can retard and inhibit the hardening process. Therefore due to the organic nature of the feed stream it was decided to add sodium metasilicate that counteracts this effect and improves the curing process. The consumption of water was difficult to predict as it is taken up by the Portland cement, the sodium metasilicate and the sorbent compounds in varying amounts.

Prior to and parallel with the actual tests as described in Table 4-2 and in Section 4.1.5, screening tests were conducted to determine the maximum sorption capacity of the silica/crumb rubber mix and investigate potential gas evolution during curing of the Portland cement.

4.1.3 Maximum Sorption Capacity

Screening tests were carried out to determine an "apparent maximum" sorption capacity of the base case crumb rubber/silica sorbent. Once the maximum capacity was established the effects of changing the sorbent ratios could be investigated.

In order to determine the maximum sorption capacity, the neutralent simulant was added and mixed with the sorbent until a thick viscous paste was formed. This experiment applied the sorbent mixture as shown in Table 4-3. Three further mixtures were prepared using progressively less neutralent simulant. All sorption mixtures were allowed to stand overnight in tightly closed jars.

Table 4-3 - Sorbent Composition for Gas Evolution Experiments

Component	Wt%
Fumed Silica	31.5
Granular Silica	23.3
Crumb Rubber	45.2
TOTAL	**100.00**

The next day the four mixtures were visually inspected. The results are shown in Table 4-4. All mixtures that contained freestanding liquid or could be poured were regarded as containing more simulant than could be adsorbed. The maximum ratio of simulant to sorbent that passed the free liquid criteria was found to be a 9.4:1 weight ratio. Subsequent stabilization and solidification test compositions were planned in the range of two-thirds to one-third of the apparent maximum sorption ratio.

Table 4-4 - Apparent Maximum Sorption Screening Tests

Test No.	Description			Results
	Simulant Wt in g	Sorbent Wt in g	Sim./ Sorb. Ratio	
AMA 1	49.9	3.7	13.5 : 1	Free standing liquid – Fail
AMA 2	45.3	3.7	12.2 : 1	Free standing liquid – Fail
AMA 3	40.0	3.7	10.8 : 1	Free standing liquid – Fail
AMA 4	34.9	3.7	9.4 : 1	Dry solid – Pass

4.1.4 Potential Gas Evolution

The objective of this screening test was to determine the pressure and composition of the gas that evolves when stabilizing the simulant in concrete after adsorbing it onto a crumb rubber/silica mixture. The sorbent composition for this gas pressure experiment is given in Table 4-3. This is identical to the base case stated in Table 4-2.

An amount of simulant equal to two thirds of the apparent maximum sorption (see Section 4.1.3 for further details) was added along with sufficient water to produce a viscous mixture. This was allowed to stand over night, before it was incorporated into concrete using the base case composition indicated as in Table 4-5.

Table 4-5 - Concrete Composition for Gas Evolution Experiment

Component	Wt%
Portland Cement	23.9
Sodium Metasilicate	7.7
Sorbent (Table 4-3)	7.0
Simulant	43.8
Lime	1.0
Water (Total)	16.6

The concrete mixture was then filled into a pipe section fitted with a pressure gauge and valve (Figure 4-1). The pressure inside the pipe section began to increase immediately and reached 20 psig after eight days.

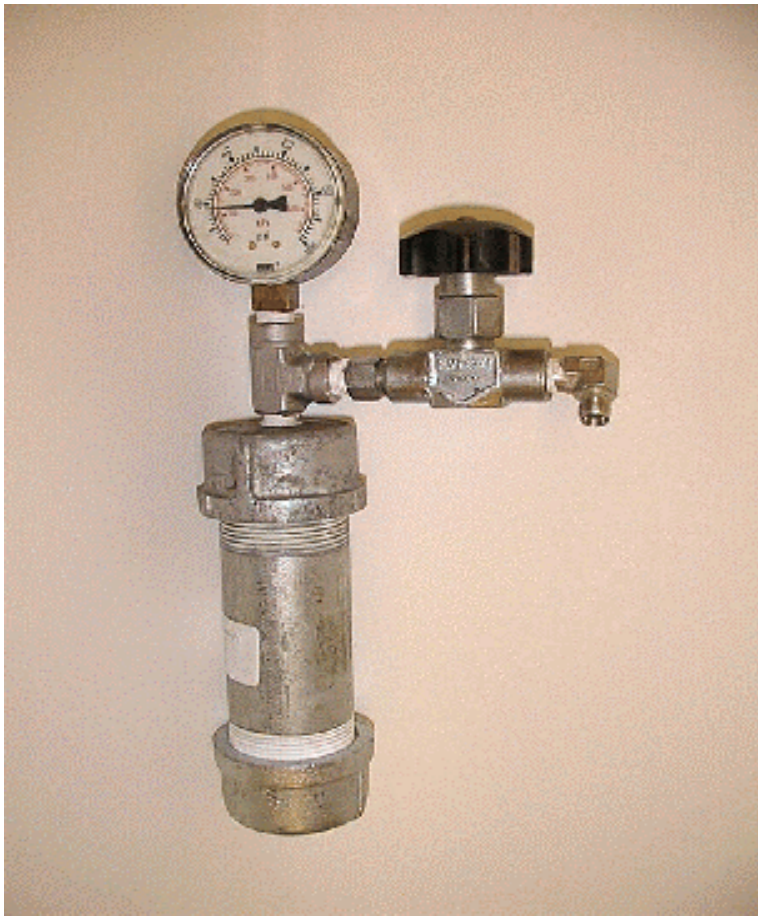


Figure 4-1 - Pipe Section with Pressure Gauge and Valve

One of the possible products of base hydrolysis of chloroform could be carbon monoxide[9]. A small sample of gas from the pipe section was withdrawn to undergo a preliminary Gas Chromatography (GC) analysis. The results indicated that chloroform was present at about its vapor pressure, together with small quantities of hydrogen, methane and ethanol, an additive in laboratory grade chloroform.

The peak area provided by oxygen was found to be 35%, which is higher than the peak area due to nitrogen measured at 32%. Since oxygen has the same elution times as carbon monoxide, it can only be concluded that the incorporation of the simulant into concrete causes the evolution of gas, which could be oxygen and/or carbon monoxide. The results of the GC analysis are summarized in Table 4-6 below.

Table 4-6 - GC Analysis of Headspace

Component	Concentration (peak area)
Oxygen + Carbon monoxide	35%
Nitrogen	32%
Chloroform	24%
Hydrogen	4%
Methane	3%
Other (small unidentified peaks)	2%
TOTAL	100%

The nature of the gas evolved was not further investigated as other experimental results indicated that this approach was not successful. (see Sections 4.1.5.3 and 4.1.5.4)

4.1.5 Complete Stream Solidification/Stabilization Tests

4.1.5.1 Preparation Procedure for Sorbent Mixture

With the apparent maximum sorption capacity for the simulant/sorbent mixture established (@ 9.4:1), retention between the different sorbent formulations could be compared. It was decided to use two-thirds and one-third of the apparent simulant maximum for the variations of sorbent to be investigated. The two-thirds point was selected for the base case. Due to the possible reaction between lime and chloroform, the lime initially included in the test plan was left out of the first exploratory sorbent mixture. If sufficient sorption of the chloroform could be achieved, then it would be considered to add the lime directly to the concrete mix in the later experiments. Excess lime in addition to the ferric oxides stabilize the +5 oxidation state and therefore decrease the solubility of the arsenic compounds in water.

The samples were prepared by premixing the sorbent materials in a glass jar, followed by adding the RRS RED neutralent simulant. The products were kept in a closed container to prevent evaporation and allowed the simulant to adsorb overnight. Details on the different compositions of the sorbent, which reflect the ratios are given in Table 4-7.

4.1.5.2 Preparation Procedure for Concrete Mixture

After the successful sorption, as defined in Section 4.1.3, the sample was crumbled and incorporated into a mixture of Portland cement, metasilicate and water to complete solidification/stabilization. This final step was designed to establish an effective ratio of those three components to the sorbent/simulant mixture that results in a stable sample. The concentrations used for these experiments, which were determined based on the test matrix shown in Table 4-2 are detailed in Table 4-7. It should be noted that Sample E3 was planned to have a low lime concentration, however as lime was not a variable included in this first set of experiments the sample was not prepared. Sample E4 was planned as a low simulant case,

but had to be discarded due to an error in the composition. The values shown in this table are the actual values, therefore there are slight deviations from the intended ratios.

Table 4-7 - Composition of First Exploratory Experiments using Non-As Simulant

Component	Concentration in Wt%						
	Base Case	**High G Silica**	**High Sim**	**High Silica**	**High Rubber**	**High P. Cement**	**Omit NaMS**
Experiment No.	**E1**	**E2**	**E5**	**E6**	**E7**	**E8**	**E9**
Sorbent [a)]	7.7	7.1	5.8	6.7	6.9	6.6	8.8
Simulant	48.4	45.8	55.1	43.4	42.0	41.7	56.5
Sorbent & Sim.	56.1	52.9	60.9	50.1	48.9	48.3	65.3
NaMS [b)]	7.8	7.4	8.3	7.2	6.8	8.2	0.0
Water	18.8	21.7	12.1	27.0	28.8	18.1	17.1
Portland Cement	17.3	18.0	18.7	15.7	15.5	25.4	17.6
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Sorbent Composition							
Fumed Silica	31.0	19.6	31.4	33.9	27.1	31.5	29.4
Granular Silica	23.4	33.9	23.0	26.8	18.6	23.3	22.1
Total Silica	52.6	53.5	54.4	60.7	45.7	54.8	51.5
Rubber	45.6	46.5	45.5	39.2	54.3	45.2	48.5
TOTAL	100.0	100.00	100.0	100.0	100.0	100.0	100.0

a) Sorbent mixture as indicated under "Sorbent Composition" in the table

b) NaMS – Sodium Metasilicate (Na_2O_3Si)

The components were mixed in a disposable beaker to form a viscous paste, which was placed into a plastic bag. The plastic bag was chosen to facilitate sample recovery from the pipe at the end of the curing period. The sample in the plastic bag was inserted into 4 inch long, threaded pieces of nominal 1.5 inch, schedule 40, galvanized pipe for curing. The pipe molds were sealed with Teflon™ tape to minimize any loss of volatiles during the curing process, as they could potentially be a source of hazardous air pollutants including VOCs. Each recipe produced a concrete sample weighing approximately 200 grams, which was cured in a single pipe mold as shown in Figure 4-2 below.

Figure 4-2 - Pipe Molds for Sealing Concrete Mixtures during Cure

4.1.5.3 Complete Stream - First Set Test Results

The results of the first simulant experiments are shown in Table 4-8. All products except composition E7 (high rubber) contained some free liquid. Only two products, E7 and E2 (more granular, less fumed silica) hardened to a solid, the rest showed a soft texture.

Another observation was that the water addition required to prepare the concrete mixture was relatively high. SwRI assumed that this could have been due to water being adsorbed onto the crumb rubber/silica mixture. This could be detrimental if the water displaced the organics from the sorbent.

Table 4-8 - Sorption & Portland Cement – First Batch

Test No.	Description	Observation	Results
E 1	Base Case	Soft texture, free standing liquid	Fail
E 2	Low Fumed Silica : Granular Silica	Hard texture, free standing liquid	Fail
E 3	Low Lime	Planned but not performed following screening test results (see Section 4.1.5.1)	
E 4	Low Simulant	Sample discarded due to error during preparation	
E 5	High Simulant	Soft texture, free standing liquid	Fail
E 6	High Silica	Soft texture, free standing liquid	Fail
E 7	High Rubber	Hard texture, no standing liquid	Pass
E 8	High Portland Cement	Soft texture, free standing liquid	Fail
E 9	Omit Sodium Metasilicate (NaMS)	Soft texture, free standing liquid	Fail

4.1.5.4 Complete Stream - Second Set - Test Procedure & Results

For the second set of solidification experiments, the procedure was modified to investigate the possibility of water displacing the already adsorbed organic compounds. In the first set of tests (Section 4.1.5.3), the dry concrete components were mixed and then combined with the simulant/sorbent mixture. Sufficient water was then added to ensure a smooth viscous paste. For this set of tests a smooth concrete mixture was prepared before adding the simulant/sorbent mixture. This was carried out rapidly in an attempt to minimize possible displacement of the organic compounds by water. Apart from that modification, the samples were prepared following the procedures described in the previous section for the first set of tests.

Details of the composition of samples for the second set of tests are given in Table 4-9. A "Zero Case" was included without any simulant to establish whether the sorbent/concrete mixture is suitable for solidification/stabilization.

Table 4-9 - Composition of Second Exploratory Experiments

Compositions of Second Exploratory Trials using Non-As Simulant, Wt%										
Concrete Composition										
Component	**Zero Case**	**Base Case**	**High P. Cement**	**High Simulant**	**Low Simulant**	**High Rubber**	**High Silica**	**High G. Silica**	**Low NaMS**	**Low Lime**
Experiment No.	**E10**	**E11**	**E12**	**E13**	**E14**	**E15**	**E16**	**E17**	**E18**	**E19**
Sorbent[a)]	58.8	7.8	7.1	5.7	14.4	8.0	7.9	7.9	8.6	7.9
Simulant	0	50.9	44.5	53.1	44.5	50.8	50.8	50.9	53.9	50.9
Sorbent & Sim.	58.8	58.7	51.6	58.7	58.9	58.8	58.7	58.8	62.5	58.8
NaMS[b)]	8.0	8.0	8.1	8.0	8.0	8.0	8.0	8.0	8.0	8.0
Water	12.3	12.3	14.3	12.3	12.3	12.2	12.3	12.2	10.8	12.2
Portland Cement	21.0	21.0	26.0	21.0	21.1	21.0	21.0	21.0	21.0	21.0
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Sorbent Composition										
Fumed Silica	23.0	23.0	23.0	23.0	23.0	17.6	27.2	16.3	23.0	24.4
Granular Silica	17.0	17.0	17.0	17.0	17.0	13.4	20.8	21.8	17.0	18.7
Total Silica	40.0	40.0	40.0	40.0	40.0	31.1	48.0	38.1	40.0	43.1
Rubber	50.0	50.0	50.0	50.0	50.0	61.3	39.5	51.4	50.0	52.5
Lime	10.0	10.0	10.0	10.0	10.0	7.7	12.5	10.5	10.0	4.3
TOTAL	100.0	100.00	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

a) Sorbent mixture as indicated under "Sorbent Composition" in table

b) NaMS – Sodium Metasilicate (Na_2O_3Si)

The results from the second set of tests are shown in Table 4-10. None of the samples had a solid consistency, most even showed standing liquid. It was decided not to submit these samples for further analysis.

Table 4-10 - Sorption & Portland Cement – Second Batch

Test No.	Description	Observation	Results
E 10	Zero Case – no simulant	Not concgealed to monolith, soft texture	Fail
E 11	Base Case	Soft texture, standing liquid	Fail
E 12	High Portland Cement	Soft texture, standing liquid	Fail
E 13	High Simulant	Soft texture, standing liquid	Fail
E 14	Low Simulant	Soft texture, standing liquid	Fail
E 15	High Rubber	Soft texture, standing liquid	Fail
E 16	High Silica	Soft texture, standing liquid	Fail
E 17	High Granular Silica Conc	Soft texture, standing liquid	Fail
E 18	Low NaMS	Soft texture, standing liquid	Fail
E 19	Low Lime	Soft texture, standing liquid	Fail

4.1.6 Path Forward for S/S of Entire Stream Experiments

After reviewing all the results for this phase of the test program it was decided to discontinue with the approach of treating the entire neutralent stream as success appears to be highly unlikely. Therefore the route of distillation followed by separate solidification/stabilization of the top and the bottom fraction, was pursued.

4.2 Distillation

The distillation/separation experiments were carried out using actual RRS RED neutralent, which was supplied to SwRI from Deseret Chemical Deport in Utah. For this second approach, the experimental effort was made to remove a chloroform rich fraction by distillation while arsenic and lower volatility organic components remain in the bottom fraction. The initial objective of the distillation was to separate the chloroform in order to conduct analytical testing on the chloroform free fraction to determine the composition of the RRS RED neutralent stream and the distribution of the arsenic. Ultimately the objective was to determine whether significant improvement in stabilization and disposal volumes could be achieved by separate stabilization of the two fractions.

After separation, the arsenic containing bottom fraction was solidified by the “two-step” method applied in the first part of the program, while the chloroform was incorporated into a polymeric structure using the Friedel Craft Reaction. The final step for this approach was to combine the two stabilized products for solidification in concrete, following the procedure in Section 4.1.5.4. This approach is presented diagrammatically in Figure 4-3.

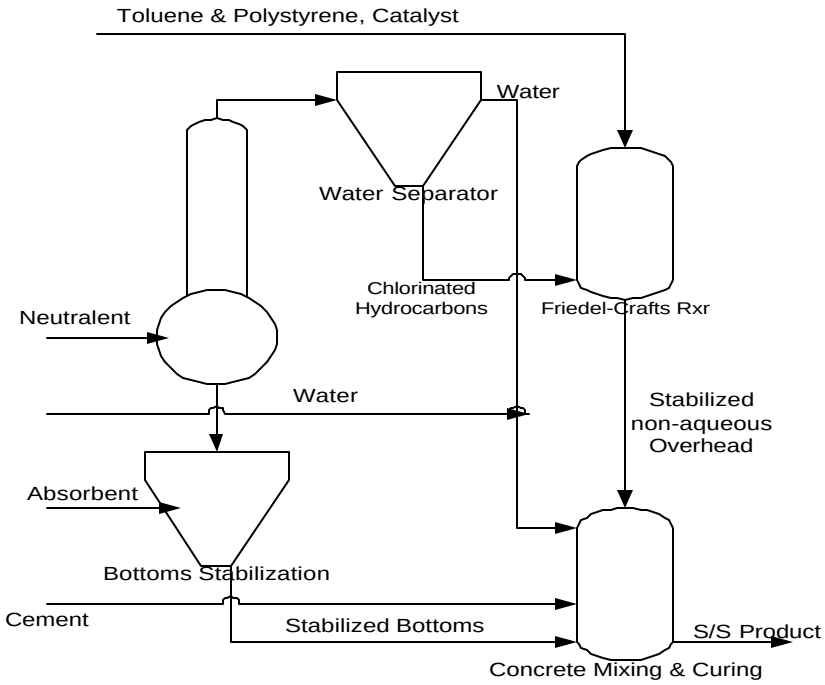


Figure 4-3 – Flowdiagram of Distillation & Solidification/Stabilization Process

4.2.1 Separation by Distillation

Prior to the separation of the two fractions, a distillation (ASTM D 86) was carried out to determine the temperature profile of the RRS RED neutralent components. This would also provide information about the distribution of the arsenic species, which is important to the solidification effort. Based on the data obtained from the distillation, a suitable cut off point for the separation of chloroform from the remaining neutralent could be determined for the subsequent experiments.

4.2.1.1 Distillation Test Description

SwRI received two gallons of RRS RED neutralent for these experiments. Samples taken from the top and the bottom of the shipping container indicated that the neutralent was uniform except for a thin film on the top of the liquid. For these experiments pipettes were used to withdraw the sample.

For the distillation, 1.0 liter of neutralent was charged to the kettle and the reflux splitter was set to provide a reflux to product ratio of 7 to 1. The overhead fraction of the distillation was collected in a chilled receiver in small increments until 70% had been distilled overhead. Figure 4-4 shows the overhead and bottoms distillation temperatures from the distillation of the 1.0 liter of neutralent. Photographs of the distillation equipment set-up can be found in Appendix A. When 70% had been distilled overhead, it was apparent from the temperature record that the chloroform rich phase had all been distilled overhead. This was confirmed by later analysis.

Figure 4-4 – Distillation Temperature Profile

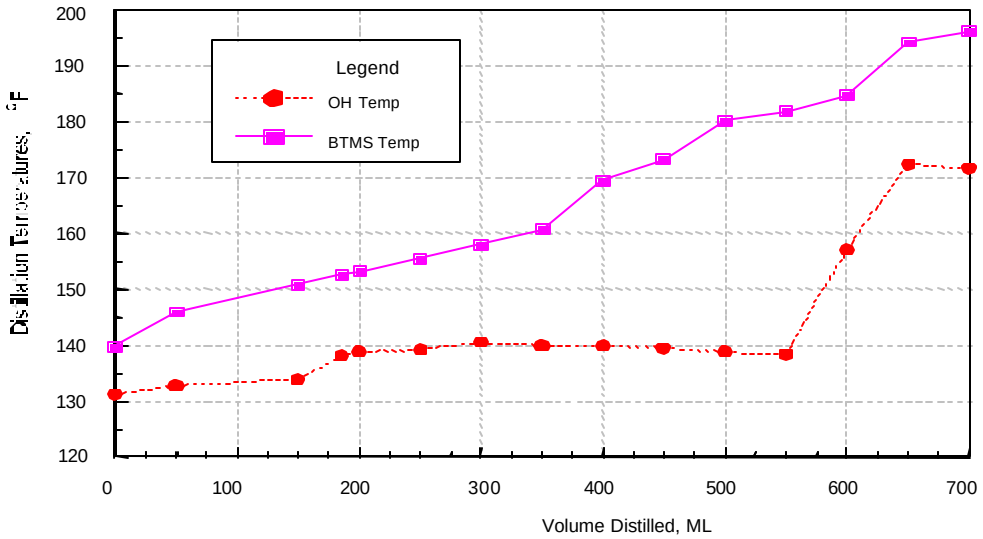
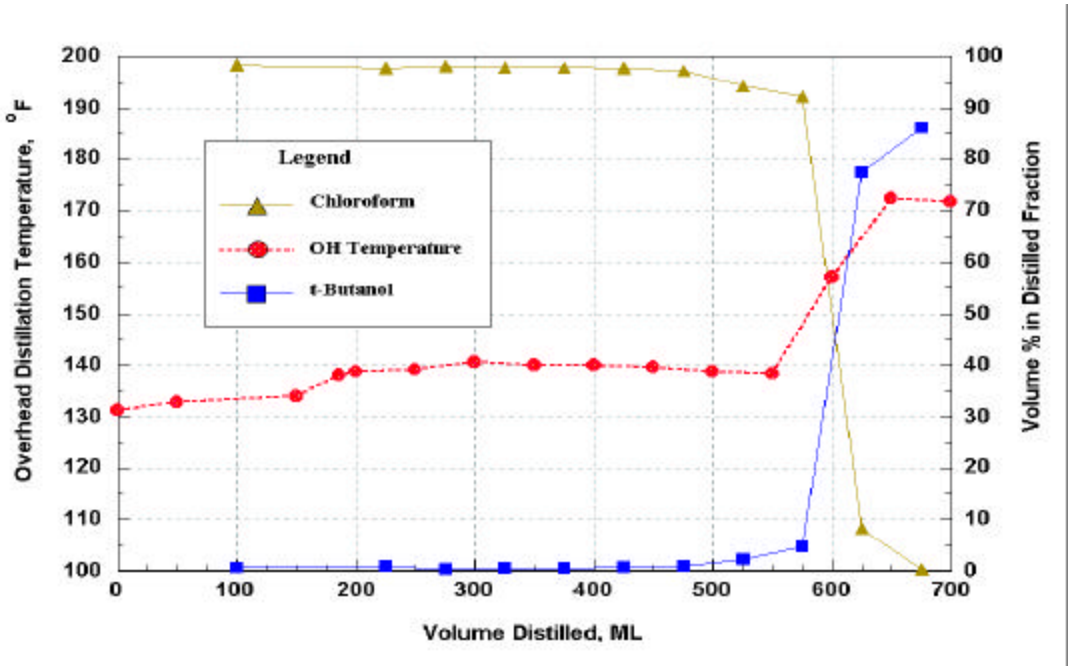


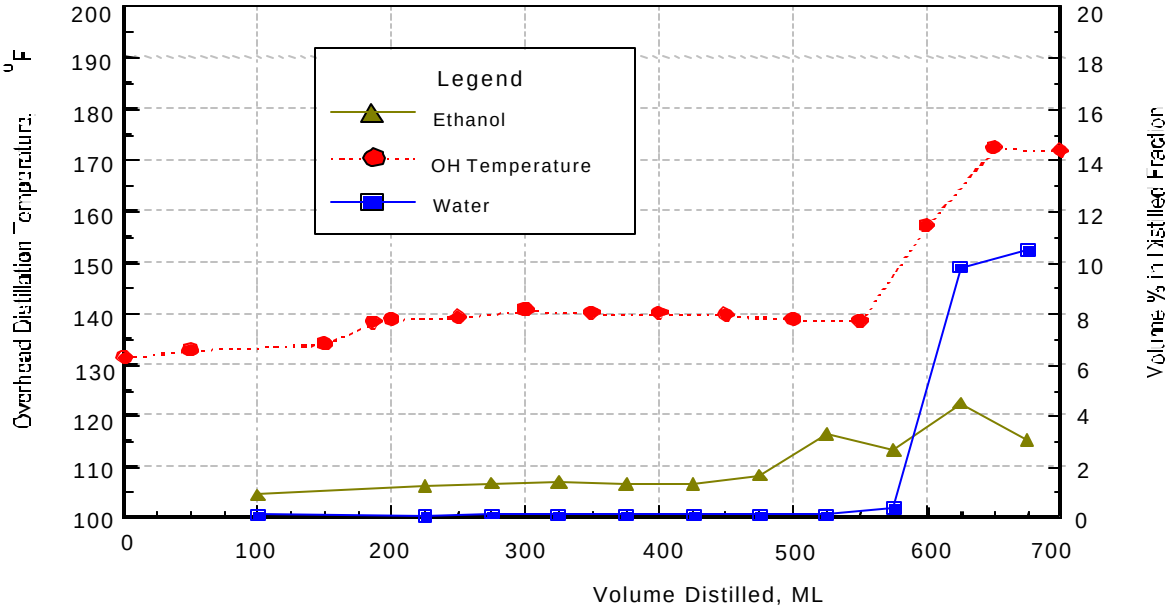
Figure 4-5 shows the concentrations of chloroform and t-butanol in the non-polar portion of the overhead fractions from the neutralent distillation.

Figure 4-5 – Composition of Non-polar Neutralent, Chloroform & t-Butanol



A polar fraction, or aqueous phase, was present in all the overhead samples. The two phases were segregated using a separatory funnel. The quantities of the polar fractions collected up through 60% are shown in Table 5-4. The aqueous, polar phase contained small amounts of chloroform and tert-butanol until the chloroform rich phase was distilled off. As the distillation continued, the fractions between 60 and 70% of the total consisted of a single phase, rich in t-butanol. Figure 4-6 shows the concentrations of water and ethanol in the non-polar portions of the overhead fractions. No arsenic was detected in any of the non-polar overhead fractions, with a minimum level of detection of 0.05 ppm by weight. In addition, two polar fractions below 25% overhead were also analyzed for arsenic with negative results using a minimum detection limit of 0.1 ppm. Arsine is the most volatile of the common arsenic compounds, therefore if present or generated during the distillation it would be expected to show up in the lightest fractions. However, arsine would not be thermodynamically favored in the presence of a strong chlorination agent, so it was not expected in this reaction. The absence of arsenic in any overhead fraction allowed easier handling than required for the bottoms.

Figure 4-6 – Composition of Non-polar Distillation Fractions, Ethanol & Water



The distillation samples for the stabilization/solidification experiments were prepared by combining selected fractions of the distillation cuts. A proportional part of each overhead, non-polar fraction up to and including the 55 to 60% fraction was taken for the stabilization sample. All of the higher boiling fractions, 60% and above, were combined for the neutralent composite bottoms fraction except for a small subsample for GC/MS analysis.

4.2.2 Stabilization/Solidification of Bottom Fraction

This experiment was designed to measure the bottom simulant retention when incorporated into the Portland cement mixture using the "two step" method.

4.2.2.1 Bottom Fraction – Simulant

While awaiting the delivery of the actual RRS RED neutralent it was decided to perform some preliminary experiments using a bottom fraction simulant. The simulant composition was an approximation of what was expected to remain in the bottom fraction after the removal of the chloroform. In order to simplify the handling of the simulant, arsenic was not included for these preliminary experiments. The composition of the bottom fraction simulant is shown in Table 4-11 below.

Table 4-11 - Bottoms Fraction Simulant Composition

Component	Wt. %
Tert-Butanol	69.93
1-Chlorobutane	5.00
1,3-Dichloro-5,5-dimethylhydantoin	15.01
Ethanesulfonylchloride	3.50
1,1,1-Trichloroethane	6.17
Tetrachloroethylene	0.39
TOTAL	100

Both the concrete composition and the mixing procedure were modified according to the findings in the earlier experiments to provide a higher proportion of the cement and to allow for sufficient water to ensure that the simulant/sorbent mixture consisted of totally wetted particles in a smooth paste. Details of the different compositions used are given in Table 4-12. The simulant was mixed with the sorbent prior to adding the required amount of water. After leaving the mixture to set overnight, the concrete samples were prepared and placed into plastic bags, which were sealed into the pipe molds for curing. (See 4.1.5.2 for further details).

Following a ten day curing period, the pipe sections were opened. All samples had hardened and none showed any standing liquid. Examples of the cured samples can be found in Figure 4-7, Figure 4-8 and Figure 4-9.

Table 4-12 - Compositions of Simulant Bottom Fraction for S/S Experiments (Wt%)

Experiment No.	**E 20**	**E 21**	**E 22**	**E 23**	**E 24**	**E 25**	**E 26**	**E 27**	**E 28**
Experiment Type	Zero Case	Base Case	High P. Cement	High Sim/Sorb.	Low Sim/Sorb.	High C. Rubber	High Silica	High G Silica	No NaMS
Sorbent Composition									
Fumed Silica	22.90	22.80	23.10	23.10	23.00	19.70	27.60	15.80	23.00
Granular Silica	17.00	17.10	16.90	17.00	17.00	14.60	20.60	24.20	17.00
Total Silica	39.9	39.9	40	40.1	40	34.3	48.2	40	40
Crumb Rubber	50.10	50.00	49.90	50.00	49.90	57.10	39.90	49.90	50.00
Lime	10.00	10.10	10.10	9.90	10.10	8.60	11.90	10.10	10.00
SUBTOTAL Sorbent	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Simulant/Sorbent Mixture									
Sorbent	28.80	21.30	18.80	16.30	23.40	21.20	18.70	24.70	22.80
Simulant Bottoms Fraction	0.00	40.00	35.50	61.30	22.10	40.00	35.00	46.40	43.00
Water	71.20	38.70	45.70	22.40	54.50	38.80	46.30	28.90	34.20
SUBTOTAL, Sim/Sorb Mix	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Concrete Compositions									
Simulant/Sorbent Mix	47.78	26.05	16.69	20.07	37.18	24.38	26.79	22.82	40.10
Fumed Silica	3.15	1.27	0.72	0.76	2.00	1.02	1.38	0.89	2.10
Granular Silica	2.34	0.95	0.53	0.56	1.48	0.75	1.03	1.36	1.55
Crumb Rubber	6.89	2.77	1.57	1.64	4.34	2.95	2.00	2.81	4.57
Lime	1.38	0.56	0.32	0.32	0.88	0.44	0.60	0.57	0.91
Simulant Bottoms Fraction	0.00	10.42	5.92	12.30	8.22	9.75	9.38	10.59	17.24
Water, Sorb.	34.02	10.08	7.63	4.50	20.26	9.46	12.40	6.60	13.71
Water, Con.	18.62	22.86	24.69	23.79	18.65	22.36	22.10	22.87	17.91
Total Water	52.64	32.94	32.32	28.29	38.91	31.82	34.50	29.47	31.62
NaMS	4.85	7.60	7.82	8.32	6.66	7.89	7.61	8.04	0.00
Portland Cement	28.74	43.49	50.81	47.83	37.51	45.37	43.50	46.26	41.99
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Figure 4-7 - Simulant Bottoms S/S Product, Base Case

Figure 4-8 - Simulant Bottoms S/S Product, High Silica Composition

Figure 4-9 - Simulant Bottoms S/S Product, "No Sodium Metasilicate" Composition

4.2.2.2 Bottom Fraction – Neutralent

Sorbents used for the solidification/stabilization of this neutralent feed stream were prepared following the same method established in the test matrix to explore the effects of the most important variables. The compositions of the sorbent and composite bottoms are detailed in Table 4-13. The composite bottom fraction of the neutralent contained a solid material, which was assumed to be tert-butanol. However when the composite bottoms fraction was added to the sorbent mixtures and allowed to stand overnight, many of the products were not as viscous as the typical stabilization products prepared earlier using the simulants.

The bottom fraction/sorbent mixture was stabilized in concrete together with the polymerized top fraction. Details of that final step are discussed in Section 4.2.3.5

Table 4-13 - Compositions of Distillation Bottom Fraction for S/S Experiments (Wt%)

Experiment No.	**E 31**	**E 32**	**E 33**	**E 34**	**E 35**	**E 36**	**E 37**	**E 38**
Experiment Type	Base Case	Low NCB	NaMS	Low NCB, NaMS	High Silica	High Silica, Low NCB	High Silica, NaMS	High Silica, low NCB NaMS
Sorbent Composition								
Fumed Silica	26.65	27.63	27.43	27.60	30.64	30.69	30.41	30.75
Granular Silica	23.04	20.38	20.43	20.43	22.80	22.70	22.61	22.59
Total Silica	49.69	48.00	47.87	48.04	53.44	53.39	53.02	53.34
Crumb Rubber	38.79	40.07	39.98	39.95	33.31	33.26	33.47	33.43
Lime	11.52	11.93	12.15	12.01	13.26	13.35	13.52	13.23
SUBTOTAL Sorbent	100	100	100	100	100	100	100	100
Neutralent/Sorbent Mixture								
Sorbent	12.76	17.52	12.43	17.57	12.37	17.54	12.43	17.53
Neutr. Composite Btm Sample	87.24	82.48	87.57	82.43	82.43	82.46	87.57	82.47
Water	As required	As required	As required	As required	As required	As required	As required	As required
SUBTOTAL, Neutr./Sorb. Mix	100	100	100	100	100	100	100	100

4.2.3 Solidification/Stabilization of Top Fraction by Polymerization

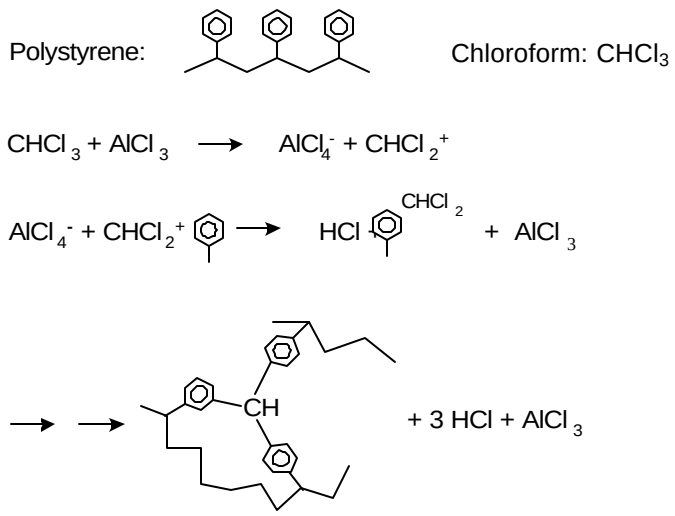
The polymerization of the chloroform was carried out after the separation. The intention was to incorporate the chloroform containing top fraction into a polymeric (polystyrene) structure. This approach was believed to have potential due to the lack of water in the neutralent. For most waste streams, an approach involving a reactive polymer would not be considered because the volatile organic compounds are usually minority components in an aqueous matrix that may also contain nonvolatile compounds and suspended solids. In this case, however, the concentrated chloroform was expected to react with a polymer to form a higher molecular weight, lower volatility product that would be easier to stabilize.

Several possibilities exist for stabilizing the chloroform fraction, i.e. the top fraction of the distillation, by chemical reaction. The Friedel-Crafts reaction with polystyrene was tested as part of the preliminary simulant tests. The advantage of this polymer is the high molecular weight and the low environmental impact.

4.2.3.1 Friedel-Craft Reaction

The chemical reaction of chloroform with polystyrene involves the crosslinking of polystyrene using the Lewis acid aluminum chloride ($AlCl_3$) as the catalyst (Figure 4-10). Friedel-Craft reactions are normally accomplished by adding the catalyst to the anhydrous hydrocarbon liquid, then stirring in the chloride. Since the catalyst is moisture sensitive and the hydrocarbon is a solid, it was attempted to solubilize the polystyrene in part of the chloroform, then add the catalyst premixed with the remaining chloroform to keep the catalyst submerged and away from atmospheric contact. The reaction generates hydrochloric acid and can be driven toward completion by removing hydrochloric acid (gas) in a calcium oxide trap.

Figure 4-10 - Anticipated Friedel-Craft Reaction for Cross-Linking Product



4.2.3.2 Polymerization Procedure for Simulated Top Fraction

While awaiting the shipment of the actual RRS RED neutralent, preliminary tests were performed using laboratory grade chloroform as a simulant of the top fraction.

In the first experiment, the polystyrene was dissolved in chloroform, prior to adding the aluminum chloride catalyst. An immediate color change indicated that a reaction was occurring, however the extent was limited as the catalyst powder did not disperse very well into the polymer solution and formed clumps. In a second experiment, the catalyst was added to the chloroform before adding and dissolving the polystyrene. This approach resulted in the same problems.

For the next experiment, the catalyst was added to toluene prior to mixing it with the polystyrene. This resulted in a good dispersion of the catalyst, which remained during the addition of polystyrene. After the polystyrene had dissolved, the chloroform was added. The mixture was boiled gently for several hours with a reflux condenser; this causes the HCl to evaporate and be retained in the calcium hydroxide trap. The removal of HCl from the polymeric solutions ensured that most of the chloroform had reacted. After cooling, the product had a viscous rubbery texture. (see Figure 4-11)

Figure 4-11 - Chloroform Incorporated in Polymer

This procedure was also used for the top fraction of the distillation of the actual RRS RED neutralent.

4.2.3.3 Incorporation of "Simulant" - Polymer into Portland Cement

The purpose of this experiment was to determine how well the chloroform that had been stabilized in polystyrene and toluene could be incorporated into a Portland cement matrix. A small amount of Portland cement was mixed with water to form a smooth viscous paste.

Then an equal volume of the stabilized chloroform polymer was added. The two fractions mixed easily and the product appeared viscous enough to hold its shape. It was molded against the side of a disposable beaker and covered to minimize evaporation.

After four days the mixture had not changed its shape and cured to a hard smooth consistency resembling plastic. The water shown in Figure 4-12 was added after the curing process to illustrate the structure of the stabilized mixture.

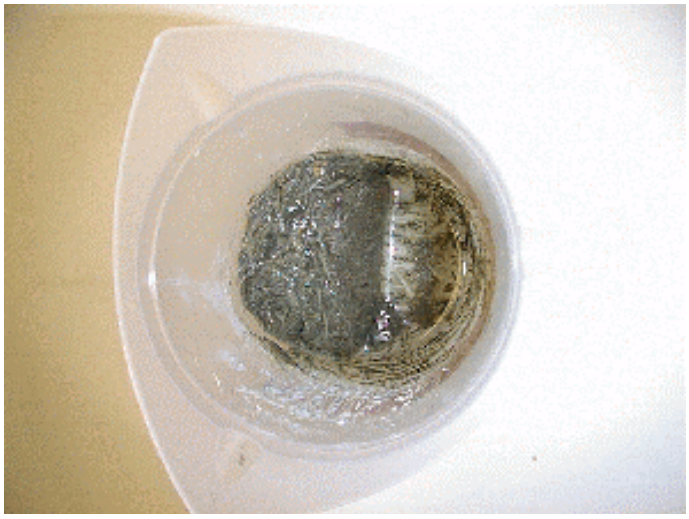


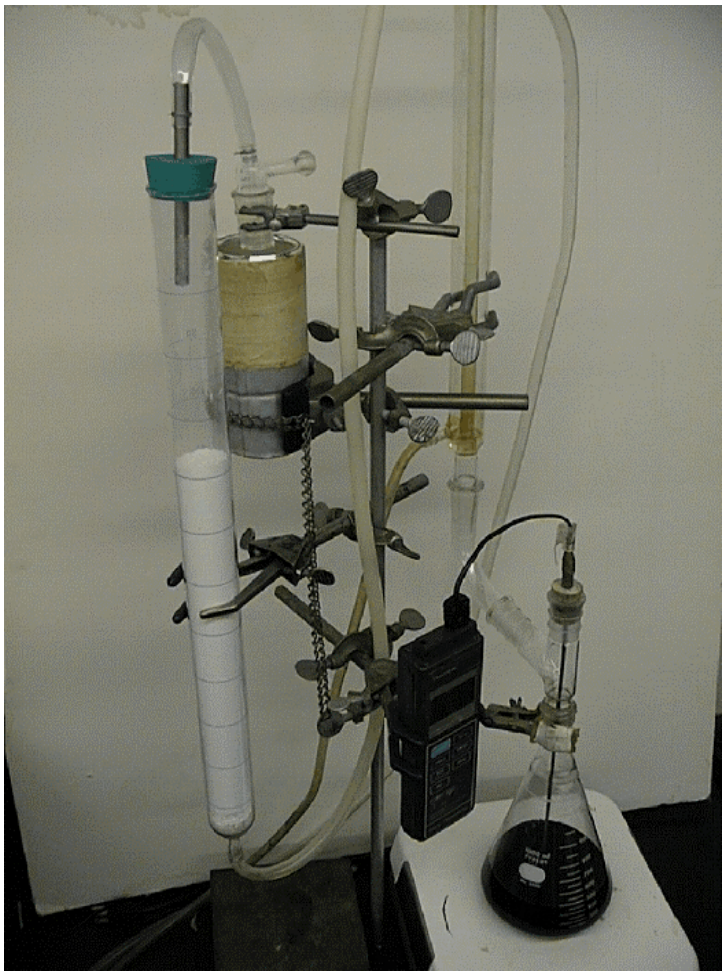
Figure 4-12 - Mixture of Stabilized Chloroform in Concrete

4.2.3.4 Polymerization Procedure for RRS RED Neutralent Top Fraction

The Friedel-Crafts reaction was performed in a flask fitted with a condenser and trap as shown in Figure 4-13. The reactor feed consisted of the non-polar overhead fraction, polystyrene beads, toluene, and aluminum chloride catalyst. The toluene and catalyst were added to the reactor first, then the polystyrene which was dissolved while stirring at approximately 135°F for about three hours. Although the mixture was visibly (but gently) boiling only trace quantities of condensate were apparent in the trap. After the dissolution of the polystyrene was complete, the non-polar overhead fraction was added, and the temperature was raised gradually to maintain slow bubbling. After about three hours, the temperature reached 160°F and the heater was turned off.

It had not been anticipated that the reaction should proceed to stoichiometric completion, however if the overhead fraction had contained pure chloroform and the reaction had gone to completion, the weight gain should have been about 147 grams. The stabilization product had a high viscosity and a low volatility, so the goals of this reaction were achieved. SwRI believes that greater cross-linking during the Friedel-Crafts reaction could be achieved to yield a better product.

Figure 4-13 – Stabilization of Non-Polar Overhead Fraction of Neutralent



4.2.3.5 Stabilization/Solidification of both fractions in Portland Cement

With completion of both the overhead and bottoms stabilization, the components were solidified in Portland cement. Each concrete sample included both the stabilized bottoms fraction and a portion of the stabilized overhead fraction. The quantity of stabilized overhead fraction in each mix was approximately proportional to the amount of bottoms fraction so each sample would contain the stabilization products of the whole neutralent. The compositions of the organic, solidified trial concrete samples is given in Table 4-14. The amounts of polystyrene, toluene, and catalyst were consolidated and called "overhead stabilizer" in the table.

Table 4-14 - Composition of Distilled Neutralent Trial Solidification Samples (Wt%)

Case	Base	Lo NCB [a]	NaMS [b]	Lo NCB, NaMS	Hi Sil [c]	Hi Sil, Lo NCB	Hi Sil, NaMS	Hi Sil, Lo NCB, NaMS
Experiment No.	**E 31**	**E 32**	**E 33**	**E 34**	**E 35**	**E 36**	**E 37**	**E 38**
Portland Cement	24.3	25.1	29.7	30.2	24.4	25.4	29.9	31.0
Water	10.2	10.6	17.1	18.0	10.3	10.8	16.7	18.1
Bottoms Sorbent	1.8	2.5	1.3	1.9	1.8	2.6	1.3	1.9
Neutralent Bottoms	12.3	11.8	9.2	8.8	12.4	12.1	9.2	9.0
Overhead Stabilizer	35.5	35.6	26.2	25.1	35.3	33.9	26.3	24.3
Neutralent Overhead	15.9	15.5	11.7	11.2	15.8	15.2	11.8	10.8
Sodium Metasilicate	0	0	4.7	4.8	0	0	4.8	4.9
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

a) NCB – Neutralent Composite Bottoms Fraction
b) NaMS – Sodium Metasilicate
c) Sil - Silica

4.3 Solidification/Stabilization of Oxidized RRS RED Neutralent

Following the completion of the persulfate oxidation tests[10] for the RRS RED neutralent it was decided to investigate solidifying the liquid effluent from the process. The analytical data from the persulfate test program indicated that the arsenic remained in the liquid and was oxidized to the +5 state. Solidifying arsenic salt (+5) in aqueous solution is a well established process, even applied to arsenic from the destruction of chemical weapons.

With the organic matter absent from the three oxidized samples, the arsenic was incorporated directly into the concrete. However, the properties of the sample required some modification to the typical concrete composition. As delivered, the samples had just completed oxidation using an excess of persulfate, so the arsenic was in the (+5) oxidation state, which is least likely to leach out, and remained in solution primarily because of the low pH. Ferric oxide was added to the mixture to keep the arsenic in its highest oxidation state during any possible exposure to reducing conditions. Calcium hydroxide was used to maintain a high pH in the mixture. The composition of the three oxidized trial concrete samples is given in Table 4-15.

Table 4-15 - Composition of Solidification Samples Using Oxidized RRS Neutralent

Lab ID/Neutralent ID	Concentration in Wt%		
	41/L2	**42/L3**	**43/L4**
Ferric Oxide	11.55	7.17	12.94
Calcium Hydroxide	6.09	5.89	3.37
Sodium Metasilicate	3.12	2.98	2.92
Oxidized Neutralent	42.20	44.30	45.70
Portland Cement	37.04	39.66	35.07
TOTAL	100.00	100.00	100.00

The Portland cement, ferric oxide, and lime were first weighed into a beaker, mixed as dry powder, then the aqueous, oxidized neutralent sample was added and mixed to make a smooth, viscous paste. Since the oxidized neutralent was acidic, an exothermic reaction with the lime occurred. In one sample (L2) the temperature reached a maximum137°F. The sodium metasilicate was added last and stirred rapidly to incorporate it before the mixture began to harden. The samples were immediately placed in plastic bags, which were sealed in pipe sections for curing.

Following their curing period the samples were submitted for TCLP analysis.

5.0 EFFLUENT CHARACTERIZATION

All solidified samples were initially assessed by visual inspection. Only samples that showed no standing liquid and appeared to have hardened to a solid were analyzed.

5.1 Liquid Sample Analysis

The fractions obtained during the distillation were analyzed to establish the RRS RED neutralent composition and to determine the optimum fraction separation temperature for the chloroform.

5.1.1 Analytical Results of Bottom Fraction

5.1.1.1 Major Organic Compounds

The major organic components of the combined bottoms fraction were identified by GC with a thermal conductivity detector. The entire result of the analysis is shown in Table 5-1 along with the smaller peaks that were not identified in this analysis.

Table 5-1 - Major Components in Composite Bottoms Fraction by GC

Compound	Retention Time, Minutes	Wt%
Unknown	1.64	0.081
Water	8.91	9.6
Ethanol	17.06	1.47
Unknown	20.59	0.096
Unknown	20.715	0.058
tert-Butanol	21.91	86.30
Unknown	23.39	0.15
Chloroform	23.95	1.23
Unknown	26.10	0.25
Unknown	28.11	0.18
Unknown	29.52	0.55
Unknown	32.62	0.093
Total		**100.0**

5.1.1.2 Semi-Volatile Analysis in Bottom Fraction

The analysis was carried out using a J&W Scientific 30 meter DB-5 analytical column with a 0.25 mm internal diameter. Six calibration standard compounds were analyzed in a blank check. The same compounds were used as internal standards for the sample. The mean response factor from the calibration check was used to calculate the amounts of detected analytes in the sample. Before injection, the sample was diluted to 1% in dichloromethane. The results of the GC/MS Analysis for RCRA Controlled Semivolatile and Other Identified and Unidentified Compounds are given in Table 5-2.

Table 5-2 - Composite Bottoms Fraction (40%) of RRS RED Neutralent

R.T.[c]	Name	CAS No.	Est. mg/L
6.05	2-Bromo-1-chloropropane	3017-95-6	280
6.37	Unknown	Unknown	4700
6.47	1,1,2,2-Tetrachloroethane	79-34-5	1400
6.62	Unknown	Unknown	650
7.28	(C3 Halo hydrocarbon such as trichloropropane)	Unknown	6600
7.42	Unknown Trichloro-2-methylpropene	Unknown	620
7.50	Unknown Trichloro-2-methylpropene	Unknown	460
8.78	3,3,3-trichloro-2-methylpropene	4749-27-3	1200
8.83	1,1,3,3-Tetrachloro-2-propanone	632-21-3	670
9.30	Unknown	Unknown	830
9.48	Hexachloroethane a	67-72-1	65
9.68	1,1,3,3-Tetrachloro-2-methylpropane	54833-05-5	3000
9.78	1,1,1,3,3-Pentachloro-2-propanone	1768-31-6	2000
9.93	Formic acid, 1,1-Dimethylethyl (or similar) ester	7580-85-0	540
10.53	Unknown	Unknown	560
10.95	Unknown, halogenated	Unknown	1800
11.18	Unknown, aromatic	Unknown	460
12.20	Unknown	Unknown	290
12.50	Unknown	Unknown	320
13.12	Unknown	Unknown	990
13.27	Unknown, halogenated	Unknown	240
14.18	(Similar to) 1,1,3,3-Tetrachloro-2-propanone b	632-21-3	500
16.72	1-(hydroxymethyl)-5,5-dimethyl-2,4-imidazolidinedione	Unknown	17000
18.28	Unknown	Unknown	470
19.48	Unknown	Unknown	280
26.62	bis(2-Ethylhexyl)phthalate a	117-81-7	4100

a) RCRA controlled contaminant.

b) The spectrum provides a good match, but the retention time is late. The peak at RT 8.83 is in the range expected for the compound.

c) R.T. – Retention Time

5.1.1.3 Metal Analysis in Bottom Fraction

The whole neutralent sample was also analyzed for the three metals expected to be present. The analysis was made by inductively coupled plasma (ICP) spectroscopy for arsenic, mercury, and chromium. The results are shown in Table 5-3.

Table 5-3 – Metals in RRS RED Neutralent

Metal	Concentration in ppm	Bottom Fraction Conc. (Equiv.) in ppm
Arsenic	1400	3500
Mercury	3.6	9.0
Chromium	38	95

The arsenic concentration was significantly lower than initially expected from the information in the RRS Permit Application, which states the concentration for arsenic at 0-2.6%.

5.1.2 Analytical Results of Top Fraction

The overhead fraction separated out into a polar and a non-polar fraction. Prior to the analysis the fractions were separated using a standard laboratory separating funnel. The analytical results are shown in Table 5-4.

Table 5-4 - Polar (Aqueous) Phase Collected in the Overhead Fraction

Fraction in Vol%	Non-Polar Fraction in g	Polar Fraction in g	$CHCl_3$ (Polar)[a] in Wt%	t-BuOH (Polar)[b] in Wt%
0-20	221.5	21.1	n.d.[c]	0.17
20-25	45.6	0.9	0.27	0.58
25-30	55.8	0.6	n.a.	n.a.
30-35	56.5	0.7	n.a.	n.a.
35-40	62.6	0.3	n.a.	n.a.
40-45	51.6	2.1	n.a.	n.a.
45-50	55.6	0.6	n.a.	n.a.
50-55	54.8	2.1	n.d.	2.2
55-60	42.0	9.2	n.d.	6.8

a) Concentration of chloroform in the aqueous phase.
b) Concentration of tert-butanol in the aqueous phase.
c) n.d. – non detect
d) n.a. – not analyzed

Table 5-5 - Composition of the Non-polar Overhead Fractions

Fraction	Non-Polar, grams	CHCl3, Wt%	t-Butanol, Wt%	Water, Wt%	Ethanol, Wt%
0-20 Vol%	221.5	98.4	0.65	0.104	0.85
20-25%	45.6	97.8	0.94	0.044	1.21
25-30%	55.8	98.1	0.41	0.122	1.34
30-35%	56.5	97.9	0.58	0.107	1.38
35-40%	62.6	97.9	0.63	0.114	1.34
40-45%	51.6	97.8	0.81	0.118	1.32
45-50%	55.6	97.3	0.98	0.099	1.64
50-55%	54.8	94.3	2.30	0.117	3.25
55-60%	42.0	92.3	4.75	0.334	2.63
Subtotal Non-polar	646	97.4	1.09	0.12	1.44
Subtotal*	691.4	90,97	1.12	6.57	1.34
60-65%	30.5	2.52	23.7	2.97	1.36
65-70%	33.8	0.13	29.1	3.53	1.02
* Includes the polar phase data from Table 5-4. The combined overhead fraction did not include the 60-65% or the 65-70% samples, instead, they were mixed into the composited bottoms sample.					

As can be seen from the above tables the main component of the overhead phase is chloroform as expected.

5.2 Solid Sample Analyses

5.2.1 Stabilized Simulant Bottom Fraction Samples

Following a ten day curing period the pipe sections containing the solidified simulant were opened. All samples had hardened to a solid with no standing liquid. The degree of hardness varied between the samples. All samples were submitted for TCLP analysis. The “hardness” rating of each sample together with the TCLP results are shown in Table 5-6.

Table 5-6 - Composition of Simulant Bottoms S & S Concrete and TCLP Leachate (ppm)

Experiment No.	**E 20**	**E 21**	**E 22**	**E 23**	**E 24**	**E 25**	**E 26**	**E 27**	**E28**	
Experiment Type	Zero Sim	Base Case	High P. Cement	High Sim/Sorb	Low Sim/Sorb	High C. Rubber	High Silica	High G Silica	No NaMS	Regulatory Limits (mg/kg)
Qualitative Hardness Rating (Ease of Breaking by Hand):										
Rating	Hard	Moderate	Weak	Moderate	Hard	Hard	Hard	Hard	Hard	
TCLP Leachate Analyses										
1,1,1-Trichloroethane, ppm	0.001	9.0	4.9	10.0	2.5	5.5	3.0	5.2	2.0	6.0[a]
Tetrachloroethylene, ppm	0.001	0.48	0.31	0.93	0.38	0.26	0.18	0.35	0.51	0.7[b]
tert-Butanol, ppm	0.01	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	2.6[a]
Normalized TCLP Leachate Analyses (Concentration in Leachate / Simulant Concentration)										
1,1,1-Trichloroethane	n. a.[c]	0.864	0.828	0.813	0.304	0.564	0.320	0.491	0.116	6.0[a]
Tetrachloroethylene	n. a.	0.046	0.052	0.076	0.046	0.027	0.019	0.033	0.03	0.7[b]
tert-Butanol	n. a.	0.096	0.169	0.081	0.122	0.103	0.107	0.094	0.058	2.6[a]

a) Limits according to the nonwastewater standard in the Universal Treatment Standards (40 CFR 268.48)

b) Limits according to the RCRA TCLP levels (40 CFR 261.24)

c) n.a. – not analyzed

5.2.2 Stabilized Neutralent Samples

Following a 14 day curing period, the samples for both the RRS RED Neutralent and the oxidized RRS RED Neutralent were briefly opened for a preliminary examination. Six samples of the stabilized (non-oxidized) neutralent had formed only soft gels that were easily crushed with light pressure. Only two of the high silica samples hardened sufficiently for TCLP, volatile and semivolatile analysis.

All three oxidized RRS RED neutralent samples however, cured to form a very hard solid, which were also submitted for analysis. The selected samples were placed back into the pipe molds and allowed to continue curing until reaching a total curing time of 27 days.

The samples were removed from the pipe sections and the non-oxidized stabilized/solidified samples (E-37 & E-38) were comminuted by forcing through a sieve. The oxidized stabilized/solidified samples (L-2, L-3 & L-4) were crushed with a hammer. After comminution, all the samples were extracted using a standard procedure (ZHE-volatile 1311). After extraction, the leachates had increased in basicity to pH 11, which is still below the RCRA corrosivity limit of 12.5. The leachates were analyzed for volatiles by Method 8260B GC/MS analysis. Instrumental accuracy was verified by measuring a simulant sample and a quality control sample of known concentration, and a blank. The detected volatiles analytical results, given in Table 5-7, show that chloroform and benzene concentrations exceeded the allowed limits by a large margin.

Table 5-7 - Volatiles in Leachates from Stabilized / Solidified Neutralent

Component	Concentration in mg/L					
	E-37	E-38	L-2	L-3	L-4	RCRA TCLP Limit
Vinyl chloride	n.d.	n.d.	n.d.	n.d.	n.d.	0.2
1,1-Dichloroethene	n.d.	n.d.	n.d.	n.d.	n.d.	0.7
Chloroform	750	580	n.d.	n.d.	n.d.	6.0
1,2-Dichloroethane	n.d.	n.d.	n.d.	n.d.	n.d.	0.5
2-Butanone	n.d.	n.d.	n.d.	n.d.	n.d.	200.0
Carbon tetrachloride	n.d.	n.d.	n.d.	n.d.	n.d.	0.5
Trichloroethene	n.d.	n.d.	n.d.	n.d.	n.d.	0.5
Benzene	18	14	n.d.	n.d.	n.d.	0.5
Tetrachloroethene	n.d.	n.d.	n.d.	n.d.	n.d.	0.7
Chlorobenzene	n.d.	n.d.	n.d.	n.d.	n.d.	100.0
n.d. - not detected RCRA limits according to 40CFR261.24						

The leachates were also analyzed for semivolatile organic compounds following the standard Method 8270. The gas chromatograph used a J&W Scientific™ 30 meter DB-5 analytical column with a 0.32 mm internal diameter and 0.25 micron film thickness. A six point calibration was performed for all target analytes and simulant compounds and used to calculate response factors. Internal standards and analysis standards were used to verify instrumental accuracy during the analyses. The results of the analyses for detected semivolatiles, given in Table 5-8, show that the semivolatiles were also well within the required limit.

Table 5-8 – Semivolatiles in Leachate from Stabilized/Solidified Neutralent

Compound	Concentration in mg/L					
	E-37	E-38	L-2	L-3	L-4	RCRA Limit
o-Cresol	0.02	0.02	n.d.	n.d.	n.d.	200
m-Cresol and p-Cresol	0.2	0.2	n.d.	n.d.	n.d.	200
Pentachlorophenol	0.002	n.d.	n.d.	n.d.	n.d.	100
n.d. - not detected RCRA limits according to 40CFR261.24						

The leachates from both the stabilized and solidified samples, and the oxidized and solidified samples were analyzed for metals. The analyses were made by inductively coupled plasma (ICP) spectroscopy. Instrumental accuracy was verified by the measurement of calibration standards, lab control samples, a blank and the method of additions. The results are shown in Table 5-9.

Table 5-9 – Metals in Leachate from Solidified RRS RED Neutralents

Metal	Concentration in mg/L					
	E-37	**E-38**	**L-2**	**L-3**	**L-4**	**RCRA Limit[b]**
Arsenic	0.694	0.674	<0.005 [a]	0.005	<0.005	5.0
Barium	0.28	0.282	0.195	0.235	0.193	100
Cadmium	<0.005 [a]	<0.005	<0.005	<0.005	<0.005	1.0
Chromium	0.056	0.054	0.455	0.407	0.494	5.0
Lead	<0.005 [a]	0.009	<0.005	0.018	<0.005	5.0
Mercury	0.888	0.714	<0.2 [a]	<0.2	<0.2	0.2
Selenium	<0.01 [a]	<0.01	<0.01	0.011	0.011	1.0
Silver	<0.005 [a]	<0.005	<0.005	<0.005	<0.005	5.0

a) Values preceded by the symbol (<) represent the lower limit of detection. The lower limit of detection for both barium and chromium was 0.005 mg/L.
b) RCRA limits according to 40CFR261.24

As can be seen from the table the distilled and solidified/stabilized samples did pass the TCLP requirements for arsenic and the other metals, except for mercury . The concentration of Mercury in the leachate exceeded the regulatory limit.

6.0 CONCLUSIONS

Approach 1 - Solidification/Stabilization of the Complete Neutralent Stream

The S/S of the entire neutralent stream was attempted using the "two-step" methods, in which the neutralent is initially adsorbed into a crumb rubber/silica mixture before being stabilized in concrete. Two sets of tests were conducted, which both proved to be unsuccessful. None of the solidified/stabilized samples showed a sufficiently hard texture and most of them had standing liquid. Due to the lack of success of this method applied to the entire stream no further testing is warranted at this time.

Approach 2 - Distillation

In this approach the highly volatile chloroform fraction was separated successfully from the remaining RRS RED neutralent using distillation. Both the mainly chloroform containing "overhead" fraction and the arsenic containing bottom fraction of the distillation were subsequently stabilized separately, before both being solidified in Portland cement.

Approach 2a - Solidification/Stabilization of Top Fraction by Polymerization

After the separation of the chloroform by distillation this overhead fraction was stabilized/solidified by incorporation into a polystyrene structure. The resulting polymer, which showed a high viscosity and appeared to have a low volatility, was then stabilized in a Portland cement matrix together with a proportional amount of Bottom sample. The TCLP analysis after the 27 day curing time indicated a poor retention of the chloroform. The concentrations in the leachate exceeded the regulatory limit of 5 mg/L significantly. This method is not suitable for the treatment of chloroform.

Approach 2b - Stabilization/Solidification of Bottom Fraction

The Bottom fraction was stabilized using the "two-step" method and combined with the stabilized top fraction in a Portland cement matrix. Two of the initial eight samples formed a solid and were subsequently submitted for TCLP analysis. The samples however did not pass the TCLP requirements for mercury, chloroform and benzene. The concentration in the leachate exceeded the regulatory limits. This method is therefore not suitable for the treatment of mercury containing RRS RED neutralent.

Approach 3 – Solidification/Stabilization of oxidized RRS RED Neutralent Sample

As part of a separate test program also performed at SwRI RRS RED neutralent was treated using persulfate oxidation. The analyses indicated that the arsenic stayed in the remaining aqueous liquid. Solidification/Stabilization of the oxidized RRS RED neutralent effluent showed that none of the RCRA regulated compounds including arsenic, chloroform and benzene were detectable in the leachate. As shown in Section 4.3 the solidification/stabilization of the sample only requires one simple step using Portland cement and the additives ferric oxide, calcium hydroxide sodium metasilicate, all commercially available chemicals. The process is not expected to be any different from other commercial solidification/stabilization processes using standard equipment. It was therefore demonstrated that this is a technically acceptable method for the treatment of RRS RED neutralent.

7.0 RECOMMENDATIONS

- Since the screening tests for solidification/stabilization of the entire RRS RED neutralent simulant stream were not successful, it is recommended not to investigate this option further.
- The stabilization of the arsenic-containing distillation bottom fraction as well as the polymerization of the arsenic-free overhead fraction were unsuccessful, due to the leaching of mercury, benzene and chloroform respectively. It is therefore recommended to consider a different method for the disposal of the chloroform rich overhead fraction. The solidification of the bottom fraction especially with respect to the retention of mercury should be investigated.
- If the oxidation of the RRS RED neutralent is pursued further, then the solidification/stabilization of the resulting effluent should be investigated.

8.0 ACRONYMS & ABBREVIATIONS

ACWAP	Assembled Chemical Weapons Assessment Program
As	Arsenic
ATAP	Alternative Technologies and Approaches Program
CAIS	Chemical Agent Identification Sets
CFR	Code of Federal Regulations
CWM	Chemical Warfare Materiel
DCDMH	Dichlorodimethylhydantoin
DND	(Canadian) Department of National Defence
DRES	Defence Research Establishment Suffield
EPA	Environmental Protection Agency
GC	Gas Chromatography
L	Chemical agent, Lewisite
MEA	Monoethanolamine
MMD	Munitions Management Device
n.a.	Not analyzed
NaMS	Sodium Metasilicate (Na_2O_3Si)
n.d.	Non detect
NSCMP	Non-Stockpile Chemical Materiels Program
ORP	Overarching Research Plan
PMCD	Program Manager for Chemical Demilitarization
RCRA	Resource Conservation and Recovery Act
RRS	Rapid Response System
R.T.	Retention Time
S/S	Solidification/Stabilization
SwRI	Southwest Research Institute
TCLP	Toxicity Characteristic Leaching Procedure
TOC	Total Organic Carbon

9.0 REFERENCES

[1] Defence Research Establishment Suffield (DRES), "Project Swiftsure Final Report", prepared for Research and Development Branch, Department of National Defence, Ottowa, Canada, May 1995

[2] U.S. Army Program Manager for Chemical Demilitarization, "Munitions Management Device, Version 1, Lewisite Chemistry Requirements", Volume 1 of 5, page 3-4.

[3] Rapid Response System Treatment Permit Application to the State of Utah, December 22, 1998.

[4] U.S. Army Project Manager for Non-Stockpile Chemical Materiel, "Overarching Research Plan Non-Stockpile Chemical Materiel Program", June 9, 1999.

[5] Onsite Engineering Report for Waterways Experiment Station for K061, U.S.E.P.A.,Washington, DC (1988).

[6] Jesse R. Connor and Fernley G. Smith, "Composition and Method for Immobilizing Organic Compounds in Hazardous Wastes and Solid", U.S. Patent No. 5,536,898 (July 16, 1996).

[7] Jesse R. Connor and Fernley G. Smith, "Immobilization of Low Level Hazardous Organics using Recycled Materials", in Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes ASTM STP 1240, Ed: T.M.Gilliam and C.C. Wiles, American Society for Testing and Materials, Philadelphia, pp 52-69 (1996).

[8] Jesse R. Connor, (1990) Op. Cit. pp 183-200.

[9] Dr. J. Horton, TVA, Conference Call with Stone & Webster and SwRI, June 14, 2001.

[10] "Evaluation Report for the Laboratory Scale Testing of the Persulfate Oxidation Process to Treat Chemical Warfare Materiel", Stone & Webster, February 2002

Appendix A

Distillation Set-up

Figure 1 –Apparatus Used for RRS RED Neutralent Distillation